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FOUR YEARS OF GROUND-BASED TOTAL OZONE MEASUREMENTS BY VISIBLE SPECTROMETRY IN ANTARCTICA

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ABSTRACT

Visible spectrometers SAOZ have been developed at Service d'Aéronomie for permanent ground-based ozone monitoring at all latitudes up to the polar circle in winter. Observations are made by looking at the sunlight scattered at zenith in the visible range, twice a day, at sunrise and sunset. Compared to ozone observations in the UV generally in use, visible observations in the small Chappuis bands at twilight have the advantages of being independent of stratospheric temperature, little contaminated by tropospheric ozone and multiple scattering, and of permitting observations even in winter at the polar circle. SAOZ instruments have been installed since 1988 at several stations in the Antarctic and the Arctic. More than four years data at Dumont d'Urville in Terre Adélie (67 °S) are now available. The station is generally located at the edge of the vortex in spring and therefore the ozone hole is seen there only occasionally. The lowest values (140 DU) were reported in early October 1991. According to these first regular observations throughout the whole winter ozone seems to increase in late autumn and winter. Its decay does not start before the end of August. Although of smaller amplitude than with the previous version 5 data, the ratio between the ground-based and satellite / TOMS measurements displays a systematic seasonal variation correlated partly to the sun zenith angle of observations from orbit and partly to the temperature of the stratosphere. Since ground-based measurements are always made at 90°SZA, the SZA dependence must come from the satellite data interpretation (TOMS observations are between 43° to 88°SZA). The temperature dependence could be partly due to variations of ozone absorption cross-sections in the ultra-violet used by the satellite spectrometer, and partly to a systematic seasonal cycle of the air mass factor use in the interpretation of the ground based observations. However, the last contribution appears to be too small to compensate the ozone increase in winter reported by SAOZ, which is then real.

1. INTRODUCTION

Because of its large absorption bands in the ultra-violet, total ozone has traditionally been observed from the ground since early 30's in this spectral range. Measurements are performed preferentially by looking at the direct sun or moon and additionally at the sunlight scattered at zenith. Because of contamination by tropospheric absorption and scattering at large SZA for the first method, and of the increasing altitude at which the sunlight is scattered at large zenith angle for the second, observations are limited to SZA lower than 80°. Ultra-violet measurements are therefore of little use in polar regions in late autumn and winter. Alternatively, although 100 times weaker, visible Chappuis bands can be used in these conditions, provided measurements are made at twilight when the light path is enhanced by a factor of 16 in the stratosphere and sensitive instruments are used. Visible spectrometers SAOZ were developed for this purpose. They have been installed since 1988 at several stations in the Arctic and Antarctic. More than four years of data are now available at Dumont d'Urville which allows us to investigate the evolution of total ozone in winter above the Antarctic.

2. METHOD

SAOZ is a 300 - 600 nm, .6 nm resolution spectrometer looking principally at sunlight scattered by the atmosphere at zenith (Pommereau et al., 1988). The instrument is made of a flat field grating, a 512 diode array detector and a 30° field of view limiter. Measurements are performed from sunrise until sunset, through a SZA of 93°. The data are analysed in real time and the results are transmitted by satellite collection (ARGOS).

Atmospheric spectra to be analysed are divided by a reference spectrum taken at high sun and high altitude (Jungfraujoch Observatory, Switzerland, 3600 m, noon, June 1990). The broad band signal obtained is subtracted by filtering, leaving narrow differential features which are specific of the absorbents present in the atmosphere: O_3, NO_2, H_2O, O_4 in the visible range. Slant column amounts of each are then calculated by an iterative sequential correlation to laboratory cross-sections. The small residual amount of ozone in the Jungfraujoch reference spectrum has been determined by Bouguer-Langley plot and is subtracted from the slant column.

Ozone is measured in the visible Chappuis bands between 450 and 540 nm, where broad features (10 nm large) are present (Figure 1). The amplitude of the above features at twilight is of the order of 1-2% and therefore slant column uncertainties of around 1% are easy to achieve, providing O_4 (collision induced absorption bands of O_2) and H_2O signatures which are present in the spectra around 475 and 576 nm for the first and around 505, 569 and 590 nm for the second, are efficiently removed in the iterative analysis. This is particularly true in the Antarctic where blizzard or white-outs occur frequently, giving rise to large enhancements of the optical path in the very lower troposphere.

In order to retrieve the constituent vertical total column, the slant column is divided by an air mass factor (AMF) which corresponds to the enhancement of the optical path compared

to the vertical. AMF are calculated with a simple radiative transfer model (Sarkissian, 1992) which takes into account Rayleigh and Mie attenuation as well as absorption by O_3, NO_2, O_4 and H_2O.

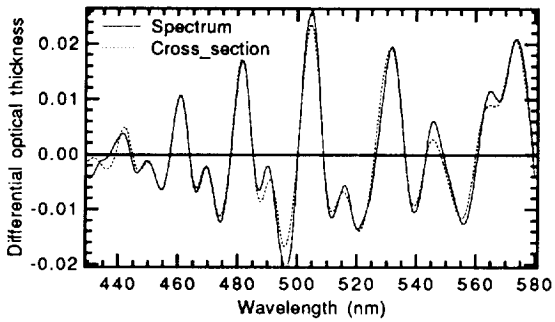

Figure 1. Ozone differential cross sections compared to an atmospheric differential spectrum recorded by SAOZ at twilight between 400 and 570 nm.

Advantages of the method are: a) the ozone cross sections are temperature independent (Vigroux 1953, Amoruso 1991), which makes measurements insensitive to stratospheric temperature variations which, at these latitudes, can be as large as 60°C within a few weeks at Spring; b) large sensitivity to stratospheric ozone at twilight due to the fact that the average scattering layer is still below the altitude of the ozone maximum. At 90° SZA, the optical path at 510 nm in the stratosphere is enhanced by a factor of 16 while the one in the troposphere remains at 1 (Figure 2). Twilight measurements in the visible are then little sensitive to tropospheric ozone. This allows daily measurements at the same geometry at twilight, all around the year at the polar circle and specially in winter.

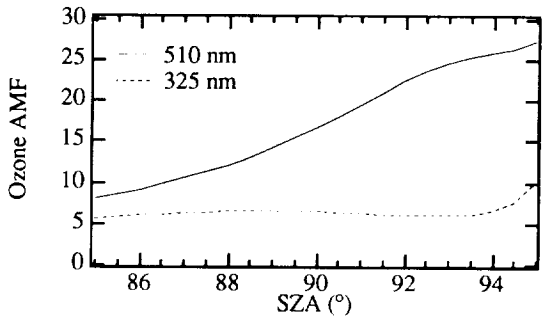

Figure 2. Ozone Air Mass Factors at twilight at 510 nm in the visible and 325 nm in the uv.

3. UNCERTAINTIES

Errors in total ozone with this method are the sum of those of the spectral analysis of the measurements (random noise, absorption cross-sections and residual amount in the reference spectrum) and those of the AMF which is used in the retrieval.

The relative contributions to the AMF uncertainty are presented in figure 3a and the error budget of total ozone versus SZA is presented in figure 3b. As the errors in the least squares correlation between signal and absorption cross-sections during a twilight period are small at one standard deviation, the random error of the measurements is 1 to 2% at 90° SZA for a single spectrum, and always less than 1% if 4 or 5 records between 87° and 91° are averaged. According to the various authors having published data since Vigroux (1953), uncertainties in the ozone absorption coefficients in the Chappuis bands are smaller than 3% and the temperature dependence is lower than the detection limit -1% - (Amoruso et al., 1990). The uncertainty of the residual amount of ozone in the reference spectrum, even if 15%, is smaller than 1% when divided by the enhancement factor at twilight.

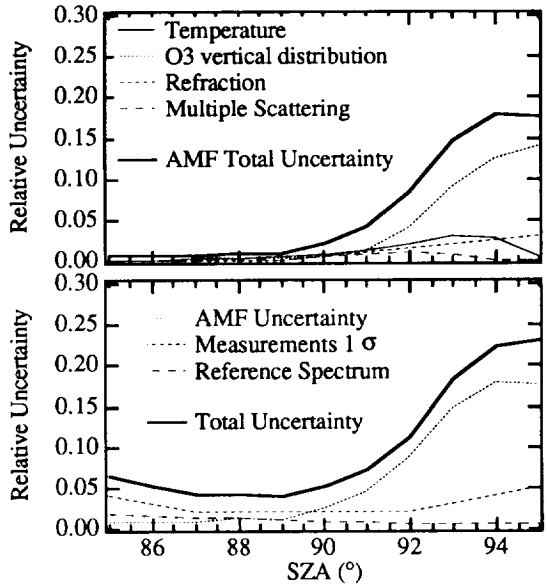

Figure 3. Error budget of total ozone measurements in the visible. a) contributions to the Air Mass Factor uncertainty; b) contributions to total ozone uncertainty.

The Air Mass factor (the optical path of the scattered sunlight into the atmosphere) depends on molecular scattering, Mie scattering by aerosols, refraction, multiple scattering and vertical distributions of the absorbing species. The simple radiative transfer model has been used to investigate the AMF sensitivity to stratospheric temperature and ozone distribution. The consequence of a warming of the stratosphere from 200 K to 250 K is to reduce the AMF by less than 3% at 90° SZA. The consequence of a lifting of the altitude of the ozone concentration maximum (summer or ozone hole compared to winter) is also to reduce the AMF. The amplitude of this effect at 90° SZA is of the order of 6 % between extreme vertical distributions. It increases rapidly at larger SZA. Between 87° and 91° SZA and for a stratospheric absorber, the air mass factor in the visible does not differ significantly if multiple scattering, refraction and albedo are taken into account (Perliski, 1991). Therefore ± 4% at 90° SZA is a good estimate of the AMF uncertainty if a constant one is used without attention given to stratospheric temperature and ozone vertical distribution. However, it must be noticed that the two corrections are in the same direction from winter to summer. They will result in a systematic seasonal variation of 8% maximum amplitude, which will lead to an underestimation of ozone in summer compared to winter, by the same amplitude. Among the relative contributions to the AMF uncertainty summarised in figure 3a, the most important one is the variability of the ozone profile.

The error budget of total ozone versus SZA is summarised in figure 3b. At low SZA, the main contributions are loss of sensitivity, tropospheric multiple scattering increasing the slant column of H_2O, O_4 and surface O_3 if any, in presence of clouds or blizzard and uncertainty in the residual ozone in the reference spectrum. At large SZA, the largest contribution is the one of the AMF uncertainty, which as seen before, is dominated by the variability of the vertical O_3 distribution. No correlation is observed, in general, between day to day fluctuations of O_3 and O_4 which is then used as an indicator of multiple scattering. Only few large peaks (less than 5 times a year during extreme white-out) appear to correlate with small O_3 peaks which can result either from tropospheric O_3 or small spectral interference. The best compromise for SAOZ is then to consider measurements only between 87° and 91°. The error budget at 90° becomes then:

- Slant column RMS (random)	2%
- Air Mass Factor (random)	4%
- Absorption Cross Sections (systematic)	3%
- Reference Spectrum Residual (systematic)	1%
-Total Precision	6%
-Total Accuracy	10%

Table 1: Error budget of total ozone

In addition to this, PSCs and aerosols can perturb the measurements. They all result in an underestimation of total ozone. The model shows that to be significant PSCs must be unusually optically dense: a 10 % apparent reduction at 90° SZA would require a vertical optical thickness of 0.1, which is rather unusual. This happens during "mini-hole" episodes, which will not be treated here. Similarly, thick volcanic aerosol layers like the one resulting from the eruption of Mt Pinatubo in 1991 reaching optical thicknesses of 0.2 or more, cause total ozone to be largely underestimated. The effect is obvious in our data at all latitudes but will not be discussed here.

4. OBSERVATIONS IN THE ANTARCTIC

Four years of continuous SAOZ measurements at Dumont d'Urville are displayed in figure 4a. They show:

- a seasonal variation with two maxima: one in late spring (November) after the ozone hole in September - October and a second in winter, which would indicate that ozone depletion does not start before the end of August;
- an average decrease by some 5% of the summer total ozone from 1988 until 1991;
- deep ozone minima in spring when the vortex approaches the station as demonstrated by variations of temperature at 50 hPa (Figure 4c), the deepest having occurred in October 1991 (140 DU);
- ozone minima lasting a few days sometimes in summer (January 1991) or autumn (May 1988, April 1990).
- a large apparent decrease of total ozone after September 1991 which result from the arrival of the aerosols layers of Mt Pinatubo and probably also from Hudson (Sarkissian et al., 1992). This event will not be discussed here.

5. COMPARISON BETWEEN SAOZ AND TOMS

The data of direct overpass measurements of the TOMS / Nimbus 7 spectrometer (Version 6) are shown in a similar plot (Figure 4 b). TOMS day to day variations are obviously highly correlated to those of SAOZ. However, the amplitude of the late spring maximum is larger, and although data are missing at SZA larger than 88°, it is clear that the TOMS displays a winter maximum of smaller amplitude. The large disagreement after September 1991, mainly due to an artefact in SAOZ observations because of the volcanic aerosols layer, will not be discussed here.

TOMS measurements are performed around noon, at high sun, at 43° to 88° SZA, depending on the season. SAOZ measurements are performed at twilight at 90° SZA. For the comparison, AM and PM SAOZ values are averaged. In fact, ozone diurnal variation is, in average, negligible except during

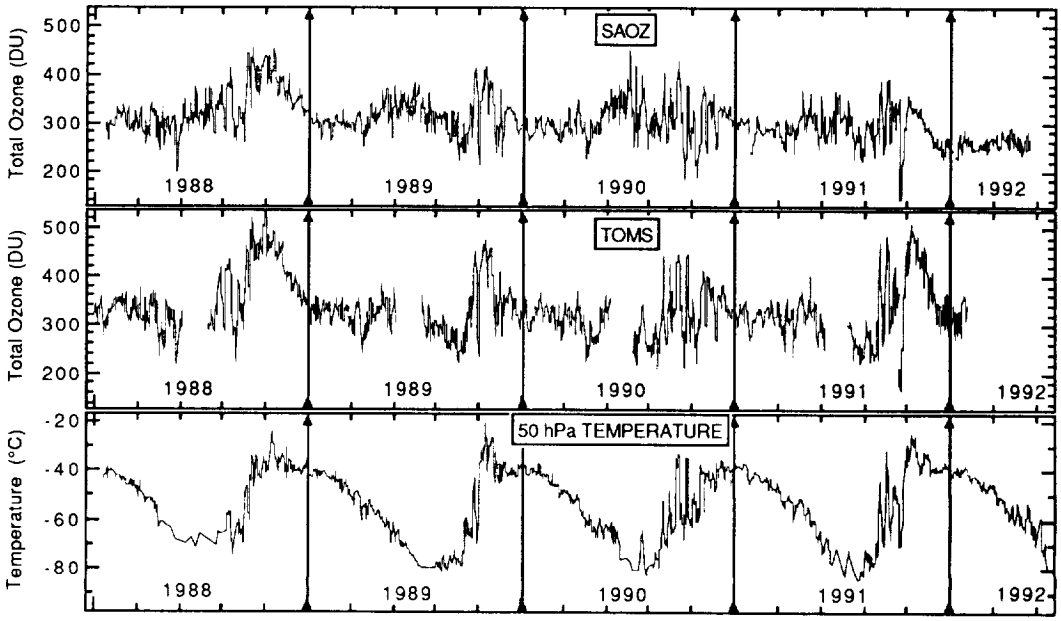

Figure 4. a) Daily twilight total ozone measured by SAOZ at Dumont d'Urville from 1988 until 1992;
b) TOMS version 6 total ozone from direct overpass measurements above the station;
c) 50 hPa temperature recorded by radio sondes.

short periods when systematic differences of the order of 0.5% may appear (Pommereau et al., 1989).

Four years of daily ratio between SAOZ and TOMS are plotted together in figure 5 as a function of day of year. A 20% amplitude systematic seasonal variation appears with a day to day fluctuation of less than ±5%. The difference is smaller in autumn (days 110-150) than in late winter (days 190-270). Although still large, the peak-to-peak 20% annual amplitude is reduced compared to the 30% observed during a first comparison using version 5 data (Pommereau et al., 1989).

A multi-parameter correlation shows that the seasonal variation between SAOZ and TOMS can be described by both a SZA and a stratospheric temperature dependence. The best fit for the SZA dependence is a parabolic law valid between 60° and 88°, ($SAOZ / TOMS = 5.5\ 10^{-2}\ SZA + 5.4\ 10^{-5}\ SZA^2$). The difference reaches 6% at 88°. The best fit for temperature is a linear dependence of $-2.9\ 10^{-3}$ /°C which would correspond to a 17% total ozone variation for a temperature range of -20°C to -85°C, typical at spring above Dumont d'Urville.

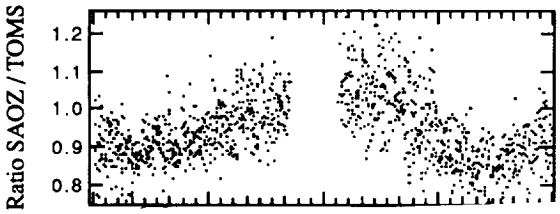

Figure 5. Seasonal variation of the ratio SAOZ / TOMS from the 4 years data as a function of day of year.

As SAOZ measurements are always performed at twilight at 90° SZA, the SZA dependence must be due to the TOMS. The total ozone underestimation at 88° is consistent with the results (6 - 12%) of a comparison between total ozone measurements at the same location in summer, at high sun from the ascending orbit and at low sun from the descending one (Stolarski et al., 1990).

The temperature dependence might partly originate in SAOZ and partly in the TOMS. It was shown earlier that a systematic seasonal variation of the SAOZ air mass factor could result from the annual variation of stratospheric temperature and ozone vertical distributions. A maximum amplitude of 8% was estimated, with the AMF smaller in summer than in winter, leading to a total ozone overestimation in winter if a constant AMF is used throughout the year. A more precise evaluation of this effect which requires modelling a monthly AMF using temperature and ozone vertical distributions, now regularly monitored at Dumont d'Urville, will be conducted next. However, if the above estimation is right, the AMF seasonal variation cannot explain more than 30 to 40% of the total difference between SAOZ and TOMS at maximum. Another explanation could possibly be the known temperature dependence of ozone absorption cross-sections in the ultra-violet. Table 2 shows the result of an estimate of the TOMS pairs dependence from newly available ozone absorption data measured at +2°C, -30°C, -45°C and -55°C (Malicet et al., 1992).

TOMS	Variation	Δ T= 65 °C variation
A pair	.00265 $°C^{-1}$	17.2 %
B pair	.00171 $°C^{-1}$	11.1 %
C pair	.00118 $°C^{-1}$	7.67 %

Table 2: Temperature dependence of the TOMS pairs

Usually, below 84° SZA (before day 120 and after day 220 at polar circle), TOMS uses the A pair. The result of a temperature dependence of the ozone absorption coefficients would be then of the order of 17 %, like the observed seasonal variation of the ratio SAOZ / TOMS between days 220 and 300. For observations closer to the terminator, the A pair weight and the B pair weight are small. The temperature dependence in winter between days 120 to 220 would be then less important (8-10%), but added to the SZA dependence.

In conclusion, both the SZA dependence and the temperature dependence result in an underestimation by TOMS of total ozone in winter in polar regions, by up to 20%, while the assumption of a constant AMF could result in an overestimation by SAOZ by up to 8%. Even if corrected by the last factor, SAOZ would display a total ozone increase in late fall and winter in Antarctica and would then indicate that ozone depletion does not start before the end of August.

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